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Development of Low-Density Silica Particles for SHIVA

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Introduction

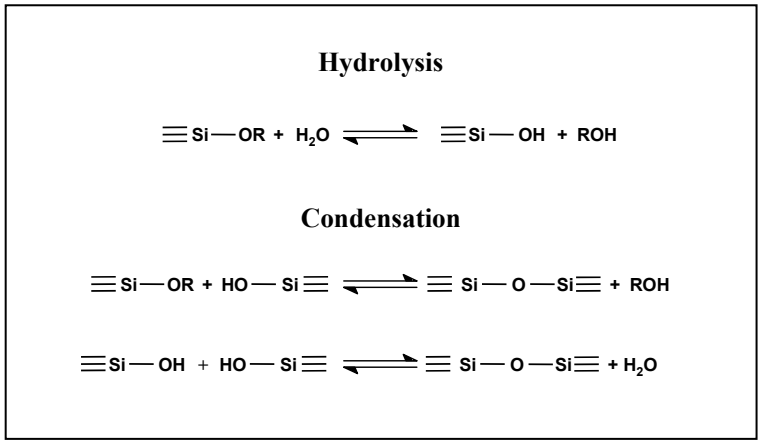
The objective of this work is the syntheses of low-density spherical silica particles, which will be used to further enhance our knowledge of the fundamental physics of the particle movements in fluids. The equations describing the particle/fluid motions have being under development and investigation over the last 100 years, yet the complete solution to this equation remained elusive, yielding only approximations and numerical solutions. Recently however, the first analytical solution to the general equation was produced by the joint efforts of NASA and NRA (Coimbra and Rangel, 1998). These particles will be used as a part of the various studies conducted to support SHIVA (Spaceflight Holography Investigation in Virtual Apparatus), the flight experiment proposed to validate this new analytical solution to the Stokes equation. The SHIVA project is designed to investigate the movement of particles in fluid and to understand and quantify the phenomena of microgravity, as well as allow the expansion of the limits associated with this analytical solution (Trolinger, J. D. 2001). The experiment proposes to use state-of-the-art holography, to precisely record the position of the particle and to allow the electronic downloading of these holograms, so that they are available on earth in real time.

Grounds experiments, utilizing tethered 2mm-diameter polypropylene particles in Krytox fluid, have being conducted and they have proven that the particle can be located with a precision sufficient to measure the effect of the history term (Trolinger, Espernace, Rangel, Coimbra et. el). Tethering the particle, allows the simulation of microgravity, however tethering the particle, produced added forces, which served to further complicate the equation. To make measurements of more general cases that cannot exist on the ground, particles with different densities are needed for the space experiment. Specifically three classes of particles are needed. Heavy particles with densities higher than the fluid, which would lag behind the fluid, particles with similar density as the fluid, which would move with the fluid, and light particles with densities less than the fluid, which would lead the fluid.

Our laboratory was charged with synthesizing the light spherical particles. This article discusses the synthesis, drying, sputtering and properties of these particles. Ideally the density of the fluid that is used in the experiment should be ten times more than the density of the particles. The fluid utilized in the experiment, Krytox, a perfluorinated polyether fluid, has an average density of 2g/cc, consequently, we would like to synthesize particles with an average density less than 0.2 g/cc. Since aerogels are highly porous, lightweight materials, with density as low as 0.003 g/cc (Physical Properties of Silica Aerogels) we decided to synthesize silica microspheres aerogels with diameters ranging from 0.5 mm to 4 mm. Aerogels are synthesized using sol-gel techniques, followed by supercritical solvent extraction, which leaves the original gel structure virtually intact.

Aerogels are open-cell polymers with pores less than 50 nanometers in diameter, as shown in figure 1. They are made by the reaction of the appropriate monomer, via the sol-gel polymerization technique, scheme 1. The monomers, which are suspended in solution, react with each other to form a sol, followed by cross-linking, which forms the sol-gel. The final aerogel is produced by carefully drying, so that the final structure does not collapse. In the case of silica aerogels, the monomeric units usually utilized are either tetramethyl orthosilicate (TMOS), Si(OCH3)4) or tetraethyl orthosilicate (TEOS, $Si(OCH_2CH_3)_4$). This is a multiple step

process involving the initial hydrolysis, where by the metal alkoxide reacts with water to form metal hydroxide (M-OH), followed by condensation, where two metal hydroxides (M-OH + HO-M) combine to give a metal oxide species (M-O-M.)



Scheme 1. Silica Sol-gel Formation.

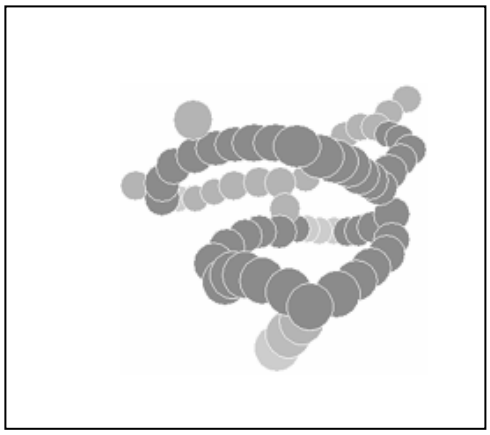


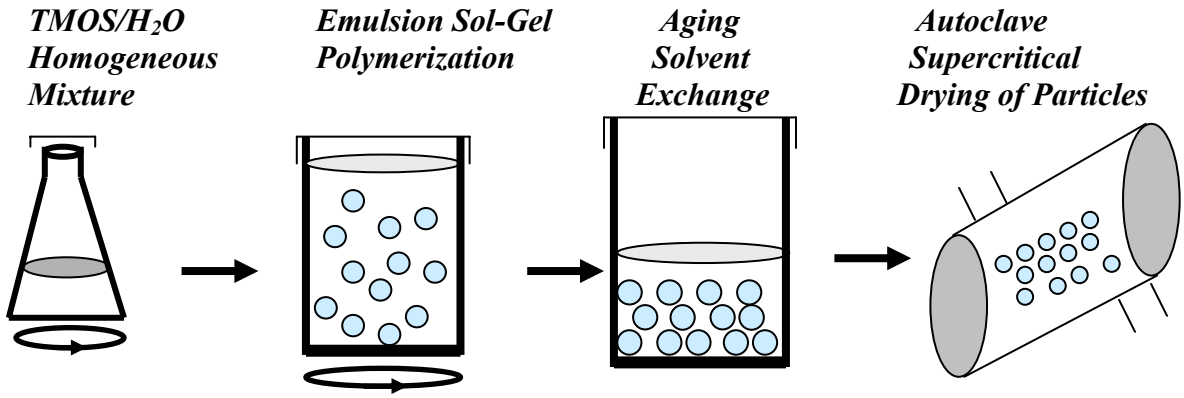
Figure 1. Aerogels open-cell

Methodology and Discussion

The aim of the research is to synthesize low-density spherical silica aerogels ranging in diameter from 0.5 to 4 mm. Once the particles are dried, via supercritical drying, they are then sputtered with gold. The sputtering serves to prevent silica pores from absorbing moisture and or other liquids, such as the Kyrtox fluid, which in turn would increase the density of the particles. The hydrolysis and polycondensation of silicates, such as tetramethyl orthosilicate (TMOS), using the sol-gel methods have been used to produce controlled monodisperse silica spheres in the micron size range (Stober, 1968). However, we wanted to make larger particles in the millimeter size range, so we modified this process.

The sol-gel process that we used consisted of the four steps (scheme 2). In the first step, we prepared a homogeneous solution, by dissolving the TMOS into deionized water. The amount of TMOS used ranged from 5 % - 25% (v/v). (It should be noted that the final density of the particles is controlled by the total amount of TMOS used.) We found out that it is very important to make sure that the initial solution was homogeneous and thus we stirred the solution for 90 minutes before proceeding to the next step. The second step involved converting the homogeneous solution into a sol. This was done via an inverse emulsion process. The homogeneous TMOS/water solution was pipetted into a mineral oil/pentane solvent mixture and then stirred until the delicate gel had formed. The size of the microspheres could be controlled by the amount of mineral oil added into the pentane, the string speed and the percent TMOS utilized. For smaller size spheres, more mineral oil was added, faster stirring speeds employed, and less TMOS used, as shown in table 1. Aging and soaking is the combined third step. In aging, the sols are reinforced and strengthened. This was accomplished by placing the delicate spheres into H_2O/EtOH solvent (1:1 v/v) for 48 hours. Soaking the particles in pure EtOH, is critical, because it serves to remove all the water in the alcogel's pores, and replaces it with ethanol. Any water left in the gel is not removed by the supercritical drying, and leads to opaque

and dense aerogel. Soaking the gels in pure EtOH and constantly replacing the bath EtOH, with new anhydrous EtOH, accomplished this step. The fourth and final step consists of the supercritical drying of the gels, which serve to remove all liquid within the gels, leaving only the solid linked silica networks. CO_2/EtOH solvent exchange, followed supercritical venting of CO_2 is the process employed in this step. The process is conducted in an autoclave.

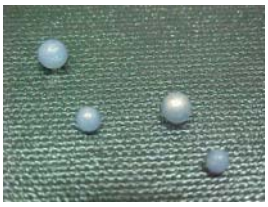


Scheme 2. The Four-Step Process of producing Spherical Silica Aerogels

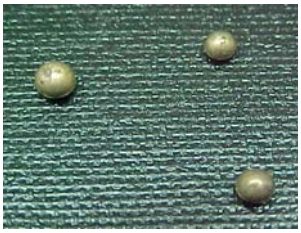
Once the particles are dried, they are then sputtered with gold. The first trial, the particles were sputtered for 200 sec, however, the resulting particles were purple, indicating that there was a very thin layer of gold on the particles. The second time, the particles were sputtered for a 1000sec, and the resulting particles were golden. Figure 2, depicts wet alcogel, dried aerogels, 200-secs gold sputtered particles and 1000-secs gold sputtered particles.

Wet-gel particles, in ethanol

Supercritically dried particle



Purple Particles: 200-sec-gold sputtered



Gold Particles:1000-sec-gold sputtered

Figure 2. Spherical Silica Particles made from 25% TMOS

Particle Properties

Density

The particle's density was calculated as follows:

The total mass of three gold particles, made from the 25% TMOS, was found to be 0.0315 g
Average mass was 0.0105 g
The average diameter of gold particles, was found to be 3.0 mm
Average radius = 1.5 mm = 0.15 cm
Volume = $4/3\pi r^3$ = 0.01413 cm^3
Density = 0.743 g/cc
The resulting density was 3 times less than the density of Krytox. This particles were made using 25 % TMOS. Ideally we would like the particle density to be 0.2g/cc. So we decided to try and make some particles using 20 % TMOS, then reducing the amount of TMOS until we get a density that closely match what we are looking for. However, the following calculations show that the density of 20% TMOS particles would closely match the density that we are aiming for;
Final Volume Fraction (f) of SiO_2 = % TMOS (V/V) * .395
For Example: 20 % TMOS
1-p = (.2)(.395) = 7.9 % SiO_2 ; Gel porosity is p = 92.1 %
$\rho(\text{aerogel}) = \rho(SiO_2)(1-p) + \rho(\text{Air})\, p = (2.2)(0.079) + (0)(.921) = 0.174$ g/cc
However, we have assumed that we have complete conversion and that there is no shrinkage during the drying process:
Now, Assume 10% Shrinkage
$\rho_{\text{shrinkage}} = \rho(\text{aerogel}) / .9 = 0.193 \sim 0.2$ g/cc.

Lyophobic Particles

The terms lyophilic (liquid-loving) and lyophobic (liquid-hating) are frequently used to describe the tendency of a surface or functional group to become wetted or solvated. If the solvent used is water, then the terms hydrophilic and hydrophobic are used. Since it is paramount to make sure that the particles are both hydrophobic and lyophobic, we tested the wetterability of both the aerogels and the gold-sputtered aerogels. Initially when the uncoated particles are placed in 10 ml of water, in a graduated cylinder, they float. However, in a few seconds, they fall to the bottom, indicating that water wets the silica particles and then the particles absorb water into the empty pores. This indicates that the surface groups of these particles are predominately silanol, Si-OH. On the other hand, both the purple particles and the gold particles float in the water, even after 5 minutes, indicating that gold converts the hydrophilic surface into a hydrophobic one.

Experimental Procedure

Silica alcogel was prepared from tetramethyl orthosilicate (TMOS, Aldrich 98 %) using a two-step process. Dissolving the appropriate amount of TMOS in water and stirring the sample for

90 minutes prepared a homogeneous TMOS sample, first step. The TMOS ranged from 5 % to 25 % (v/v) in de-ionized water. In the second, step, mineral oil and pentane were added into a 1,000 ml, glass long beaker equipped with a magnetic stir. The reaction was allowed to react, while stirring, until the gel-like particles had formed. The amount of time allowed for the second step, depends upon the % TMOS, as shown in table1. The mineral/oil pentane was decanted carefully, and the gelled particles were washed several times with H_2O and then with H_2O/ EtOH (1:1 v/v). Solvent exchange was conducted for two days, with pure anhydrous EtOH being added every 12 hours.

Sample Preparation of 25 % TMOS

2.5 ml of 98 % TMOS was added into 7.5 ml of de-ionized water and stirred for 90 minutes. 600 ml of pure mineral oil was added into a 1,000-ml long-glass beaker, equipped with a magnetic stir. 300 ml of pentane was added. The two solvents formed two layers, but after thorough stirring, a homogenous mixture was obtained. 9 ml of the 25 % TMOS was pipetted into the mixture, while stirring, and the reaction was allowed to react for 2 hours. The mineral oil/pentane was decanted and the gelled particles were washed five times with de-ionized with H_2O and three times with then with H_2O/ EtOH (1:1 v/v) mixture. Finally the particles were aged in a glass beaker for 48 hours in a water/ethanol (50/50 v/v) mixture. Then, the water/ethanol was decanted and the anhydrous ethanol was added to the particles. Every 12 hours, the ethanol was decanted and pure anhydrous ethanol was added. The solvent exchange was conducted for 48 hrs.

Results and Discussions

Low-density spherical silica particles, were prepared via sol-gel routes in which tetramethyl orthosilicate, TMOS, was hydrolyzed and condensed forming a gel, which was aged, dried under supercritical conditions and subsequently sputtered with gold. The density of the particles ranged from 0. to 0.74 g/cc depending on the amount of TMOS used in the reaction. The higher the % TMOS utilized, the higher the density, as illustrated in table 2. The gelation time, also depended on the % TMOS used in the reaction, the higher the % TMOS utilized, the less time it took to form the gel, table 2. The size of the particles depended on the amount of mineral oil used in the reaction, and the % TMOS used. The greater the quantity of mineral oil utilized, the smaller the particles. The higher the % TMOS utilized the larger the particle size. Particles with TMOS less than 10 % formed gels that were too soft. When these gels were dried, they collapsed. Particles made from the 15% TMOS constantly had bubbles in the gels, so these gels were not dried. Consequently, the densities from these particles were not determined.

Table 1. Particle Gelation Time and Density of Particles

% TMOS	Reaction Time (h)	Mineral oil: Pentane Ratio	Density (g/c)	Average Diameter Size
25	2	2 :1 (Speed = 5)	0.74 (3 particles)	3.0 mm
20	3.25	2 :1	0.28 (8 particles)	2.9 mm
15	4.0	2 :1		
10	6	2 :1		
5	22.5	2 :1		
25	3	3:1 (Speed = 7)	0.37 (8 particles)	1.5 mm

Conclusions

Low-density spherical silica particles were prepared, via an inversion emulsion polymerization process, utilizing mineral oil/pentane mixture as the reaction media, and water/TMOS homogeneous mixture as the emulsion. This four-step process involved an initial formation of a TMOS/H_2O homogeneous mixture, followed by the emulsion sol-gel formation of the particles. The amount of time required for the gelation depended upon the % TMOS, low % TMOS utilized, longer gelation times. Aging and soaking, whereby the sols are reinforces, strengthened, and all water in the alcogel is replaced by ethanol, was the combined third step. The final step was the supercritical drying of the particles, which was performed in an autoclave, utilizing carbon dioxide as the supercritical solvent. The particles were then sputtered with gold, converting them from hydrophilic to hydrophobic. This step serves to prevent the silica particles from absorbing any moisture or fluid into the pores. The density of the particles, which was controlled by the amount of TMOS utilized in the reaction, ranged from 0.74 g/cc to 0.15 g/cc.

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Future Work

During the course of the research, it was noted that it is very important to make the particles spherical. However, we were not able to control the particles shape, hence, it would be ideal, for lab to determine the reaction conditions which would provide, a good control for the particles shape. Futhermore, the lab should make particles from 12.5 and 17.5 % and determine if these particles have a density less than 0.2 g/cc.

References

Coimbra, C.F.M., and Rangel R.H. "General Solutions to the Particle Momentum Equation in Unsteady Stokes Flow. "J. Fluid Mech., (1998)

Trolinger, J.D, PI., SCIENCE REQUIREMENTS DOCUMENT: *DRAFT* , SHIVA *(Spaceflight Holography Investigation in a Virtual Apparatus),* 18 September 2001

Trolinger, J.D, Esperance, D. L**.,** Rangel R.H, Coimbra, C.F.M, Witherow, W., Rogers, J., and Ravindra, L., Small Particle Response to Fluid Motion Using Tethered Particles to Simulate Microgravity.

Stober. W. Fink, A., and Bohn, E. "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range," J. Colloid Interface Sci., 26, 62-69 (1968).

Physical Properties of Silica Aerogels, http://eande.lbl.gov/ECS/aerogels/saprops.htm